

Electronic and optical properties of two-band alloy

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The Green's function of a binary two band alloy has been worked out from the multiband theory of binary alloys of Matsubara and Yonezawa. The self energy thus obtained has been further approximated in the light of Toyozawa and Onodora's work on the one band model. This theory has been applied to a model semiconducting alloy and the divalent metallic alloy of Be and Mg in the study of their density of states and optical absorption spectra.

1. INTRODUCTION

The past two decades saw a tremendous development (Callaway 1964, Dimmock 1971, Lioucks 1964) in the theoretical study of the electronic energy states of crystalline solids and this was possible due to the inherent symmetries, point and translation, existing in their structure and the advent of fast computers. The concepts like Brillouin zone, Fermi surface and the reciprocal lattice space were the direct consequence of the translation symmetry and the various experimental effects such as de Haas-van Alphen effect, cyclotron resonance etc were the experimental manifestation of this symmetry. But in the case of disordered systems, such as alloys, the translational as well as the point symmetries disappear as a result of which the computation of the dispersion relation ($E-k$) and hence the density of states becomes extremely difficult.

However, in the beginning of the last decade it was shown by Edwards (1963) that the imaginary part of the configurationally averaged Green's function can be used to find out the density of states for the disordered system. This derivation ushered in a new era and drew the attention of a large number of workers in this line. For binary alloys two separate schools of thoughts gradually developed, the coherent potential approximation (CPA) of Soven (1966) and perturbative approach of Matsubara & Yonezawa (1966). The CPA was further improved and made more tractable through the works of Véllicky *et al* (1968), Mills (1973) and others whereas the Matsubara technique was put in a more lucid form by Yonezawa (1969) and Leath (1970) and was exploited for some model calculation by Toyozawa & Onodora (1969) and by Das & Joshi (1971). All these developments uptill now were centred on the model of one band responsible for the crystalline properties of the solid. Recently Sen (1973) have extended

the CPA to the two band model and have calculated the density of states and a few other properties of a model semiconductor. The Matsubara approach, however, is very general and contains the multiband nature in its formulation. In this work we have approximated the Matsubara-Yonezawa self energy in a more compact matrix form to calculate the density of states, mobility edges and optical spectra of a model semiconducting alloy and the divalent metallic alloy of Be and Mg.

2 MATHEMATICAL FORMALISM

For a binary alloy A - B if we regard the periodic lattice of A atoms as the unperturbed system and the random insertion of B atoms at the lattice sites as perturbation the one-electron Hamiltonian of the alloy system can be written in the form

$$H = H_0 + H_1$$

where

$$H_1 = \sum_m [V_B(\vec{r} - \vec{R}_m) - V_A(\vec{r} - \vec{R}_m)] \\ = \sum_m V(\vec{r} - \vec{R}_m) \quad \dots (1)$$

$V_A(\vec{r} - \vec{R}_m)$, $V_B(\vec{r} - \vec{R}_m)$ are the potentials on an electron at the point \vec{r} due to A and B atoms at \vec{R}_m respectively. The summation m is over impurity sites only.

We now define the one-electron Green's function for the alloy and pure unperturbed system as

$$[G(E)]_{kk'}^{ii'} = \left\langle ik \left| \frac{1}{E - H} \right| i'k' \right\rangle \quad \dots (2)$$

and

$$[G_0(E)]_{kk'}^{ii'} = \frac{1}{E - \epsilon_{ik}} \delta_{ii'} \delta_{kk'} \quad G_0^i(E, k) \quad \dots (3)$$

where $|ik\rangle$ are the Bloch functions defined as

$$|ik\rangle = u_{ik}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \quad \dots (4)$$

and ϵ_{ik} defined by the relation

$$H_0 |ik\rangle = \epsilon_{ik} |ik\rangle \quad \dots (5)$$

represents the energy of the electron in the i -th band possessing momentum k . Eq (2) defining the Green's function $G(E)$ for the alloy can be written in terms of unperturbed Green's function $G_0(E)$ and the interaction Hamiltonian H_1 as

$$[G^{-1}(E)]_{kk'}^{ii'} = (E - \epsilon_{ik}) \delta_{ii'} \delta_{kk'} - [H_1]_{kk'}^{ii'} \quad \dots (6)$$

where

$$[H_1]_{kk'}^{ii'} = \langle ik | H_1 | i'k' \rangle.$$

Expanding (6) as a perturbation series and taking the configurational average we have

$$\begin{aligned} \langle G(E) \rangle_{kk'}^{B'} &= G_0'(E, \bar{k}) + \langle G_0'(E, \bar{k}) \rangle \langle \rho_n(\bar{k} - \bar{k}') \rangle \delta_{kk'}^{B'} G_0'(E, \bar{k}') \\ &+ \langle G_0'(E, \bar{k}) \rangle \sum_{i_1 k_1} \langle \rho_{n_1}(\bar{k} - \bar{k}_1) \rho_{n_2}(\bar{k}_1 - \bar{k}') \rangle \times \\ &\times \delta_{kk_1}^{i_1} G_0^{i_1}(E, k_1) \delta_{k_1 k'}^{i_1'} G_0^{i_1'}(E, k') + \dots \end{aligned} \quad \dots \quad (7)$$

where ρ and δ are defined by the relation

$$|H_1|_{kk'}^{B'} = \rho(\bar{k} - \bar{k}') \delta_{kk'}^{B'}$$

where

$$\rho(k - k') = \sum_m e^{-i(k - k') \cdot R_m}$$

and

$$\delta_{kk'}^{B'} = \int u_{ik}^*(\bar{r}) V(\bar{r}) u_{i'k'}(\bar{r}) e^{-i(\bar{k} - \bar{k}') \cdot \bar{r}} d\bar{r} \quad \dots \quad (8)$$

Comparing eq (7) with Dyson equation we can write the matrix elements of the self energy matrix operator Σ as

$$\begin{aligned} |\Sigma(E)|_{kk'}^{B'} &= \langle \rho_n(\bar{k} - \bar{k}') \rangle \delta_{kk'}^{B'} \\ &+ \sum_{i_1 k_1} \langle \rho_{n_1}(\bar{k} - \bar{k}_1) \rho_{n_2}(\bar{k}_1 - \bar{k}') \rangle \delta_{kk_1}^{i_1} G_0^{i_1}(E, \bar{k}_1) \delta_{k_1 k'}^{i_1'} \end{aligned} \quad \dots \quad (9)$$

The above expression for self energy however does not take into account the *Exclusion Effect*. In order to incorporate it we replace $G_0(E, \bar{k})$ by $\langle G(E, \bar{k}) \rangle$ in every term of the above matrix element. Now putting $F(E) = \langle G(E, \bar{k}) \rangle$ and applying Kubo's cumulant expansion method to evaluate the configurational averages $\langle \dots \rho_{ni} \dots \rangle$ and substituting the value of cumulants (Matsubara *et al* 1966) of different order the self-energy Σ in matrix operation form is

$$\Sigma = c(1-c)\delta F_1\delta + (c-3c^2+2c^3)\delta F_1\delta F_1\delta + \dots \quad \dots \quad (10)$$

where F_1 is a diagonal matrix of n -th order and c is the concentration of B atoms in the alloy. The application of eq (10) to a real problem is restricted because of the difficulty in the proper manipulation of the infinite series. We consider a number of relevant approximations.

In one approximation the series can be terminated after a few terms such as the 4th term as was done by Das & Joshi (1971) in the case of one band. Eq. (10) then reduces to

$$\Sigma = c(1-c)\delta F_1\delta + (1-2c)F_1\delta + (1-6c+6c^2)F_1\delta F_1\delta. \quad \dots \quad (11)$$

The infinite series can however be divided into a number of partial sums which can be achieved through the diagram technique of Leath (1970) who has shown that the diagrams representing the various terms in the infinite series can be rearranged into series of terms corresponding to different types of clustering. If we however take into account terms upto double site approximations the matrix operator takes the following form

$$\Sigma = c(1-c)\delta F_1\delta \frac{1}{1-(1-2c)F_1\delta} - \frac{c(1-c)F_1\delta F_1\delta\{2-(1-2c)F_1\delta\}}{\{1-(1-2c)F_1\delta\}^2} \quad (12)$$

This is a better approximation than eq. (11) because it takes into account two complete partial sums representing two types of clustering.

On the other hand the Toyozawa-Onedora (1968) approach for one-band system can be extended to multiband system. Here instead of scalars all the terms involved will be matrices. Following the same chain of arguments we obtain the expression for the self-energy given by

$$\Sigma = \frac{c(1-c)\delta F_1\delta}{1-(1-2c)F_1\delta+F_1\Sigma} \quad (13)$$

Eqs (11), (12) and (13) are the three approximations of Σ which can be used for application to real alloys.

3 MODEL CALCULATION

With a view to applying the above formulation to an alloy of model semi-conductors and divalent metals we have resorted to a model in which the independent bands are described by parabolic density of states. The justification (Baines 1961, Wilkes 1973) of this model lies in the fact that this form of density of states curve is a well-drawn compromise between a tight-binding model and a free-electron model for the Hamiltonian of the system. Another advantage in using parabolic model is that it is free from van Hove singularities except at the band edges where they are of M and M' types. This feature makes numerical calculations considerably easier. For the pure case the density of states can be represented by

$$\rho_{11}^0 = \frac{2}{\omega^2\pi} [\omega^2 - (E - \frac{1}{2}E_g + \omega)^2] \quad \dots \quad (14)$$

$$\rho_{22}^0 = \frac{2}{\omega^2\pi} [\omega^2 - (E - \frac{1}{2}E_g - \omega)^2] \quad \dots$$

where 2ω is the bandwidth and E_g is the bandgap or overlap depending upon whether the system is a semiconductor or a divalent metal. Obviously E_g is

positive for semiconductor while it is negative in the case of metal. The 2×2 matrix Σ (Sen 1973) then takes the following form ($\omega = 1$)

$$\Sigma = \tau - \frac{1}{4} F' - F^{-1} \quad \dots (15)$$

where

$$\tau = \begin{pmatrix} E + \frac{1}{2} E_0 + 1 & 0 \\ 0 & E - \frac{1}{2} E_0 - 1 \end{pmatrix}$$

and

$$F = \begin{pmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{pmatrix}, \quad F' = \begin{pmatrix} F_{11} & -F_{12} \\ -F_{21} & F_{22} \end{pmatrix}$$

In order to evaluate F we eliminate Σ by coupling eq (15) with eqs (11), (12) and (13) and thus the following three equations result

$$c(1-c)\delta F_1 \delta [1 - (1-2c)F_1 \delta + (1-6c+6c^2)F_1 \delta F_1 \delta] - \tau + \frac{1}{4} F' - F^{-1} = 0 \quad \dots (16)$$

$$c(1-c)\delta F_1 \delta \left[\frac{1}{1 - (1-2c)\delta} - \frac{c(1-c)F_1 \delta F_1 \delta \{2 - (1-2c)F_1 \delta\}}{\{1 - (1-2c)F_1 \delta\}^2} \right] - \tau + \frac{1}{4} F' - F^{-1} = 0 \quad \dots (17)$$

$$\begin{aligned} & (\tau - \frac{1}{4} F' - F^{-1}) + \tau(1-2c)F_1 \delta - \frac{1}{4}(1-2c)F' F_1 \delta - (1-2c)F^{-1} F_1 \delta \\ & + \tau F_1 (\tau - \frac{1}{4} F' - F^{-1}) - \frac{1}{4} F' F_1 (\tau - \frac{1}{4} F' - F^{-1}) \\ & - F^{-1} F_1 (\tau - \frac{1}{4} F' - F^{-1}) - c(1-c)\delta F_1 \delta = 0 \quad \dots (18) \end{aligned}$$

where

$$F_1 = \begin{pmatrix} F_{11} & 0 \\ 0 & F_{22} \end{pmatrix}$$

The numerical solutions of eqs (16), (17) and (18) are extremely difficult until some sort of simplifications are made by imposing some strings on the nature of second order matrix δ depending upon physical conditions. Thus if we assume $\delta_{11} = \delta_{22} = 0$ and $\delta_{12} = \delta_{21}$ eq (16) can be solved and the density of states obtained for the model semiconductor of Sen (1973) are shown in figure 1. There is a striking similarity of this figure with that of P. N. Sen. If we now assume $\delta_{12} = \delta_{21} = 0$ then instead of solving eq (18) for F it is easier to solve eq (13) first for Σ and then use it to find F . As F_1 and δ both are diagonal under this assumption so they commute and the eq (13) reduces to

$$\Sigma = \frac{c(1-c)\delta^2}{F_1^{-1} + (1-2c)\delta + \Sigma} \quad (19)$$

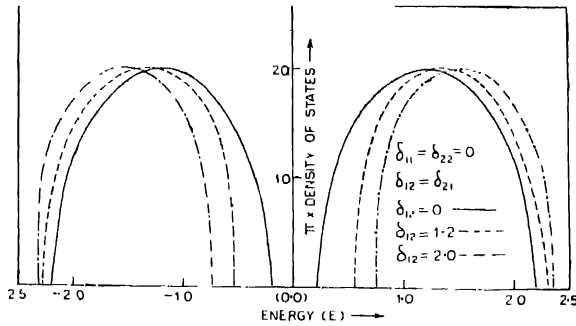


Fig. 1. Densities of states for a model semiconductor alloy for various values of δ_{12} where $\delta_{21} = \delta_{12}$ and $\delta_{11} = \delta_{22} = 0$.

With this form of F and δ , Σ also becomes diagonal with $\Sigma_{12} = \Sigma_{21} = 0$ thereby reducing eq (19) into two independent cubic equations in Σ_{11} and Σ_{22} . The positive imaginary solutions of Σ_{11} and Σ_{22} are put in the equation

$$F(E) = F^0(E - \Sigma)$$

to get the density of states from the equation

$$\rho(E) = \frac{1}{\pi} [I_m F_{11}(E - \frac{1}{2}c\delta_{11} + \frac{1}{2}(1-c)\delta_{11} - \Sigma_{11}(E)) + I_m F_{22}(E - \frac{1}{2}c\delta_{22} + \frac{1}{2}(1-c)\delta_{22} - \Sigma_{22}(E))] \quad (20)$$

The theory described above can also be applied to calculate the coefficient of optical absorption of alloys. For this purpose we make the following assumptions: (1) there is no band mixing ($\delta_{12} = \delta_{21} = 0$), (2) the transition dipole moments of the constituent atoms are equal, (3) the self energy $\Sigma(E)$ is independent of K . Under these conditions the absorption coefficient $I(E)$ is given by (Onodora *et al* 1968)

$$I(E) = \frac{1}{\pi} \left[\frac{I_m \Sigma_{11}(E)}{\{E - \frac{1}{2}c\delta_{11} + \frac{1}{2}(1-c)\delta_{11} - \text{Re } \Sigma_{11}(E)\}^2 + \{I_m \Sigma_{11}(E)\}^2} + \frac{I_m \Sigma_{22}(E)}{\{E - \frac{1}{2}c\delta_{22} + \frac{1}{2}(1-c)\delta_{22} - \text{Re } \Sigma_{22}(E)\}^2 + \{I_m \Sigma_{22}(E)\}^2} \right] \quad (21)$$

4. NUMERICAL CALCULATION

Case I - Model Semiconductor

In order to compare our results with those of Sen (1973) we have taken his example e.g. $E_g^A = 0.2$, $E_g^B = 0.6$, $\delta_{11} = 1.2$ and $\delta_{22} = 0.8$. The results of

the calculation for various values of c are shown in figure 2 ($x = 0.7$ of Sen (1973) corresponds to $c = 0.3$ of our calculation). Agreement of our calculation with that of Sen (1973) is remarkable.

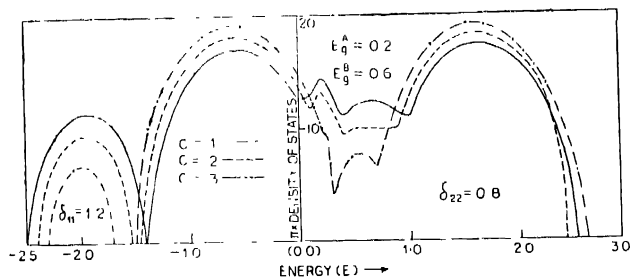


Fig. 2. Densities of states for a model semiconductor alloy with $\delta_{12} = \delta_{21} = 0$.

Case 11. Model Divalent Metallic Alloy Be-Mg

Berilium and Magnesium both possess hexagonal close-packed structure with two atoms per unit cell, thus requiring at least two complete bands to accommodate the valence electrons and the solids would be insulators. But as has been shown by various workers (Chatterjee *et al.* (1975), Anderson (1958), Falicov (1962), Torro (1964)) these are metals with overlapping bands whereby at least three bands are required to accommodate the two valence electrons. Assuming the lowermost of the three bands to be completely full we can describe the electronic phenomena of these metals by the remaining two partially filled overlapping bands. Thus the three band system can then be reduced to a two-band system enabling us to perform numerical calculation according to the formulation we developed. Coming to analyse the suitability of parabolic density of states to Be, Mg alloy we know, in case of metals where d bands are important, the density of states are better described by the tight-binding model. Although Be and Mg do not belong to this category their density of states curves, specially, that of Be are not exactly free-electron type. As the parabolic density of states describe a situation which is a compromise between tight-binding and free-electron model it will not be far from truth if we describe the metals Be and Mg by parabolic form of density of states.

In order to find out the necessary parameters for Be-Mg alloy we take a direct recourse to the data for pure Be and Mg calculated by Chatterjee & Sinha (1975) by the APW method. We have first of all counted the number of states required to fill up the lowest band, then subtracting these states from the total distribution of electron states, the other two overlapping bands are described approximately by two parabolic bands. After adjusting the width and height

of the density of states curves thus obtained to the scale of the assumed model they are shown in figure 3. As we further assume that the overlapping of bands to be more responsible than the band mixing for their notable behaviour, so we have $\delta_{12} = \delta_{21} = 0$ and the rest of the parameters follow from figure 3.

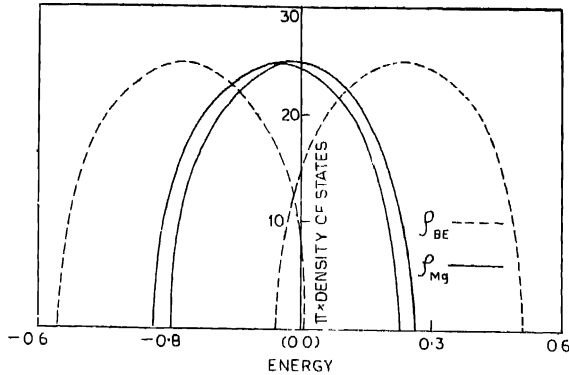


Fig. 3. Densities of states for pure Be and Mg.

$E_0^{Mg} = -1.86$, $E_0^{Be} = -0.23$, $\delta_{11} = 0.79$, $\delta_{22} = -0.84$ Ryd. The density of states $\rho(E)$ and the absorption spectra $I(E)$ have been calculated for $C = 0.1, 0.2, 0.3, 0.5, 0.7$ and 0.9 . They are shown in figures 4, 5 and 6 respectively.

Figures 4 and 5 clearly demonstrate the beautiful characteristics of the bands of the alloy. With increasing concentrations the nature of the bands shifts from pure Mg to pure Be. This is clearly evident from the maximum at the Fermi level of Mg going over to the minimum at the Fermi level of Be. These behaviours are also evident in figure 6 of the absorption spectra.

As we neglected band mixing and stressed on diagonal overlap, we can generalise the Economou & Cohen's (1970) theory to study the existence of localized states in these alloys. In that case the localization condition $L_i(E) < 1$ can be applied independently to the individual bands where we will have

$$L_i(E) = \frac{\max_K \{E^{(i)}(\vec{k})\}}{|E - \Sigma_{ii}(E)|} < 1 \quad (22)$$

for localization of an electron state with energy E in the i -th band. In numerical calculation we have taken $\max \{E^{(i)}(\vec{k})\} = \omega = 1$ and $L_i(E)$ is then easily evaluated from eq (22). It has been found that only at $c = 0.5$ there are mobility edges for both bands at the Fermi level where both the bands meet. This localized region has been shown by a thin shadowed strip.

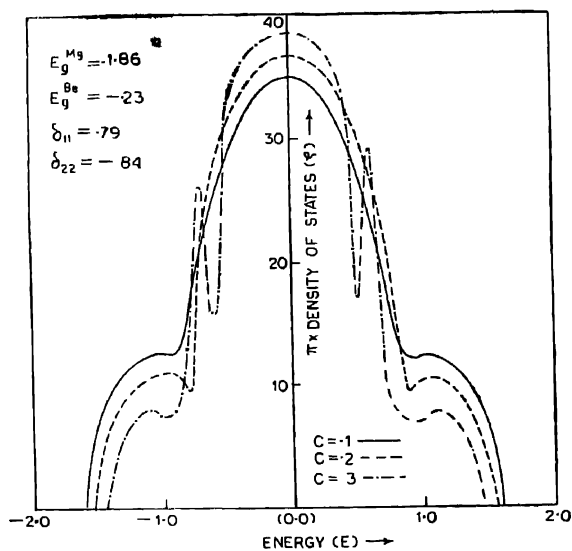


Fig. 4. Densities of states for Be-Mg alloy for concentrations 0.1, 0.2 and 0.3,

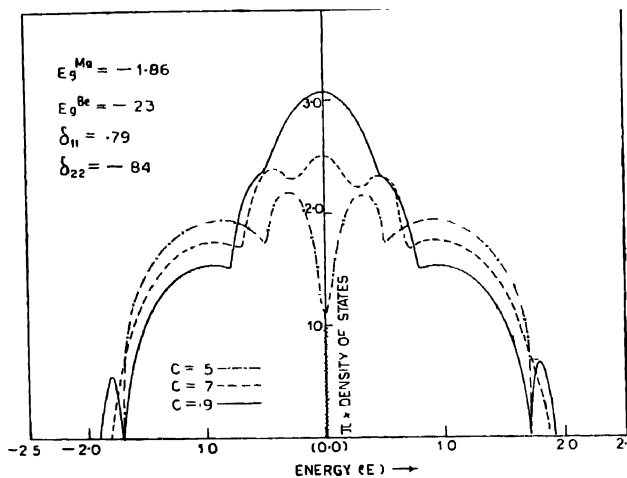


Fig. 5. Densities of states for Be-Mg alloy for concentrations 0.5, 0.7 and 0.9,

In conclusion it may be pointed out that this theory can be applied to solids involving more than two bands by increasing the dimension of the Hamiltonian. But even in third order matrix formulation with all sorts of band mixing being allowed the calculation will be extremely complicated. However, with only

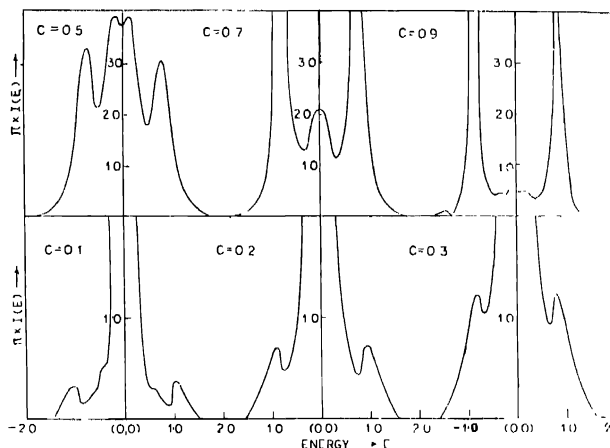


Fig. 6. Optical absorption spectra for Be-Mg alloys as a function of concentrations,

overlap present all the off-diagonal elements in δ and ω matrix vanish and the matrix equation for determining selfenergy (13) can be handled with ease. For polyvalent metals we believe overlap to be more important than interband mixing and hence the eq (13) with diagonal F_1 and δ is a good approximation for describing the electronic properties of the alloys

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REFERENCES

- Anderson P. W. 1958 *Phys. Rev.* **109**, 1492.
- Boely J. L. & Edwards S. F. 1963 *Proc. Roy. Soc. (London)* **A274**, 395.
- Callaway J. 1964 *Energy Band Theory* (Academic Press, New York).
- Chatterjee S. & Sinha P. 1975 *J. Phys. F: Metal Physics* **6**, 2089.
- Das M. P. & Joshi S. K. 1971 *Phys. Rev.* **B4**, 4363.
- Dommock J. O. 1971 *Solid St. Phys.* **26**, 103.

- Economou E. N. & Cohen M. H. 1970 *Phys. Rev. Letters* **25**, 1445.
 Fuchs L. M. 1962a *Phil. Trans. Roy. Soc.* **A225**, 61; 1962b, *Phil. Trans. Roy. Soc.* **A225**, 61.
 Louth P. L. 1970 *Phys. Rev.* **B2**, 3078.
 Lucciarollo D. C. & Economou E. N. 1975 *Phys. Rev.* **B11**, 3697.
 Loucks T. L. & Childer P. H. 1964 *Phys. Rev.* **133**, A819.
 Matsubara T. & Yonezawa F. 1966 *Prog. Theoret. Phys. (Kyoto)* **35**, 357.
 1966 *Progr. Theoret. Phys. (Kyoto)* **37**, 1346.
 Mills Robert 1973 *Phys. Rev.* **B8**, 3650.
 Onodera Y. & Toyozawa Y. 1968 *J. Phys. Soc. Japan* **24**, 341.
 Raimis Stanley 1961 *The Wave Mechanics of Electrons in Metals* (North-Holland Publishing Co., Amsterdam) p. 293-95 and 236-239.
 Sen P. N. 1973 *Phys. Rev.* **B8**, 5613.
 Soyev P. 1966 *Phys. Rev.* **151**, 539; 1967 *Phys. Rev.* **156**, 809.
 Terrel J. M. 1964 *Phys. Lett.* **8**, 149; 1966 *Phys. Rev.* **149**, 256.
 Velicky B., Kukpataek S. & Ehrenreich H. 1968 *Phys. Rev.* **175**, 747.
 Wilkes Peter 1973 *Solid State Theory in Metallurgy* (Cambridge University Press), p. 293-95.
 Yonezawa F. 1969 *Progr. Theoret. Physics (Kyoto)* **40**, 734.